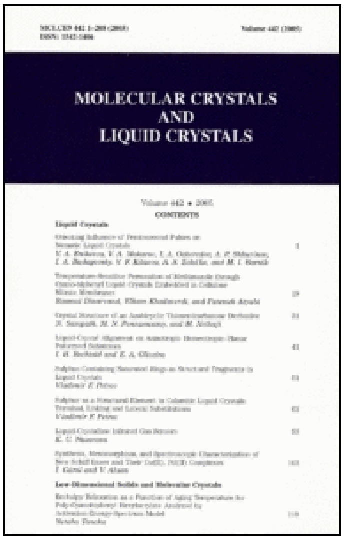

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Density and Ultrasonic Velocity Measurements in Hexyloxybenzylidene Phenylazoaniline

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The temperature variation of density and ultrasonic velocity of the liquid crystal hexyloxybenzylidene phenylazoaniline are reported. The density across the smectic A—smectic B transition is more predominant than the other transitions. The density variation with temperature and the calculated thermal expansion coefficients suggest that the transitions isotropic liquid—nematic, nematic—smectic A and smectic A—smectic B are of first order. Anomalous behaviour of ultrasonic velocity is observed across the isotropic liquid—nematic transition and prominent dips in velocity are observed at the nematic—smectic A and smectic A—smectic B transitions. The adiabatic compressibility (β_{ad}) Rao number (R_n) and molar compressibility (B) are estimated using the experimental density and ultrasonic velocity.

Keywords: hexyloxybenzylidene phenylazoaniline, density, ultrasonic velocity, thermal expansion coefficient, adiabatic compressibility, Rao number

INTRODUCTION

Increasing technological applications[1,2] of liquid crystals are attracting both physicists and chemists in understanding their basic structure. The study of density in liquid crystals provides useful information regarding various phases and phase transitions.[3–4] Ultrasonic velocity

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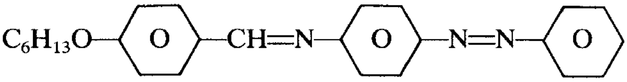
studies of the liquid crystals provide additional information and confirmation about the different phases and phase transitions.[5–7] We report here the density and ultrasonic velocity variation with temperature of the liquid crystal hexyloxybenzylidene phenylazoaniline as a part of the systematic study of the phase transitions of liquid crystals.[8–10] The phase transition temperatures of the pure compound were determined using the polarising microscope.



Hexyloxybenzylidene Phenylazoaniline

$$\text{Solid} \xleftrightarrow{104^\circ\text{C}} S_B \xleftrightarrow{125^\circ\text{C}} S_A \xleftrightarrow{147^\circ\text{C}} N \xleftrightarrow{172^\circ\text{C}} I$$

EXPERIMENTAL

H_xBPAA was prepared by condensation of equimolar quantities of *p-n*-Aminoazobenzene and *p-n*-hexyloxybenzaldehyde in refluxing absolute ethanol in presence of a few drops of acetic acid. After refluxing the reactants for four hours the solvent was removed by distillation. Crude H_xBPAA was recrystallized from ethylacetate until the constant transition temperatures were obtained.

A capillary Pycnometer with a diameter of about 0.2 mm was used for density measurements. The permitted temperature control was ±0.1°C. The level of liquid crystal in the capillary was read to ±0.01 mm with a cathetometer. The absolute error in the density measurements was $\Delta\rho = \pm 0.0001$ g/cc.

The ultrasonic velocity was measured at 2 MHz using the ultrasonic interferometer UI 601 NPL India. The cell was essentially the same as that supplied with the interferometer except a few modifications for the heating arrangement. The temperature of the cell was controlled by controlling the current flowing through the heating element surrounding the cell. The permitted temperature control was ±0.2°C. The ultrasonic velocity measurements were accurate to ±0.2%.

RESULTS

The variation of density as a function of temperature is shown in Figures 1 and 2. The thermal expansion coefficients 'α' are calculated

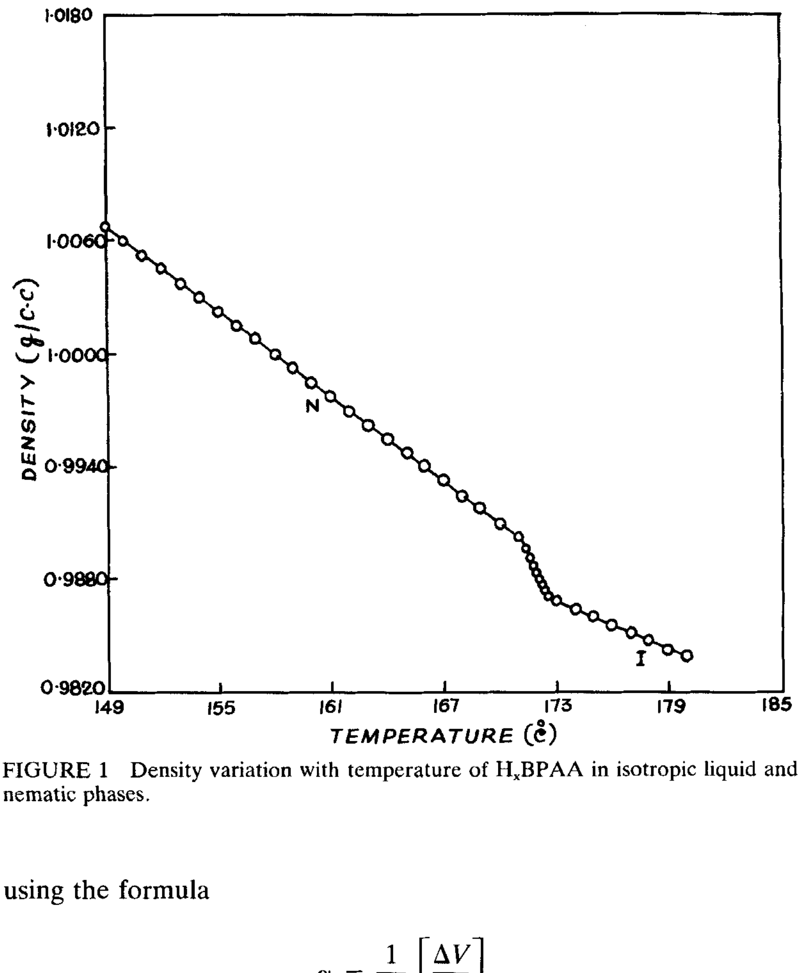


FIGURE 1 Density variation with temperature of H_xBPAA in isotropic liquid and nematic phases.

using the formula

$$\alpha = \frac{1}{V_n}\left[\frac{\Delta V}{\Delta T}\right]$$

where $V_n = (V_1 + V_2)/2$, $\Delta V = V_2 - V_1$ and $\Delta T = T_2 - T_1$; V_1 and V_2 are the molar volumes at temperatures T_1 and T_2, respectively. The variation of thermal expansion coefficients as a function of temperature is illustrated in Figure 3.

The ultrasonic velocity (V) variation with temperature is presented in Figure 4.

Specific volume (v), adiabatic compressibility (β_{ad}), Rao number (Molar sound velocity) (R_n) and molar compressibility (B) are estimated from the experimental results using the following equations.[11-12]

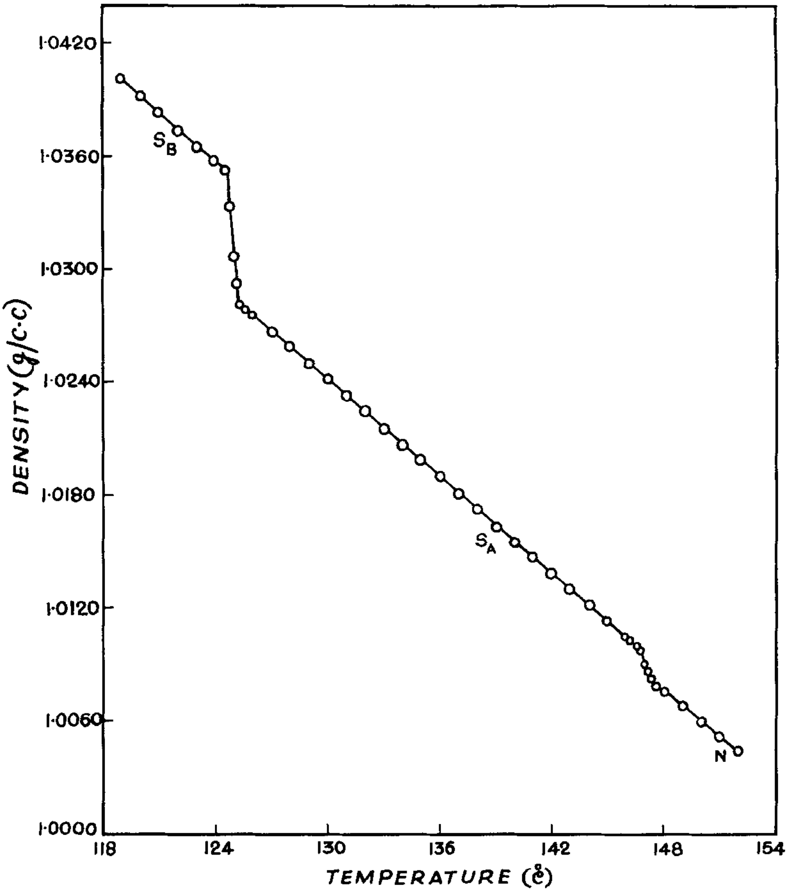


FIGURE 2 Density variation with temperature of H_xBPAA in nematic, smectic A and smectic B phases.

$$\nu = 1/\rho$$

$$\beta_{ad} = \nu/V^2, \quad R_n = M\nu(V)^{1/3} \quad \text{and}$$

$$B = M\nu/(\beta_{ad})^{1/7}$$

Where M is the molecular weight.

DISCUSSION

Density increases linearly with decrease of temperature in the isotropic liquid phase. Very near the isotropic liquid—nematic transition a sudden jump in density is observed. The thermal expansion coef-

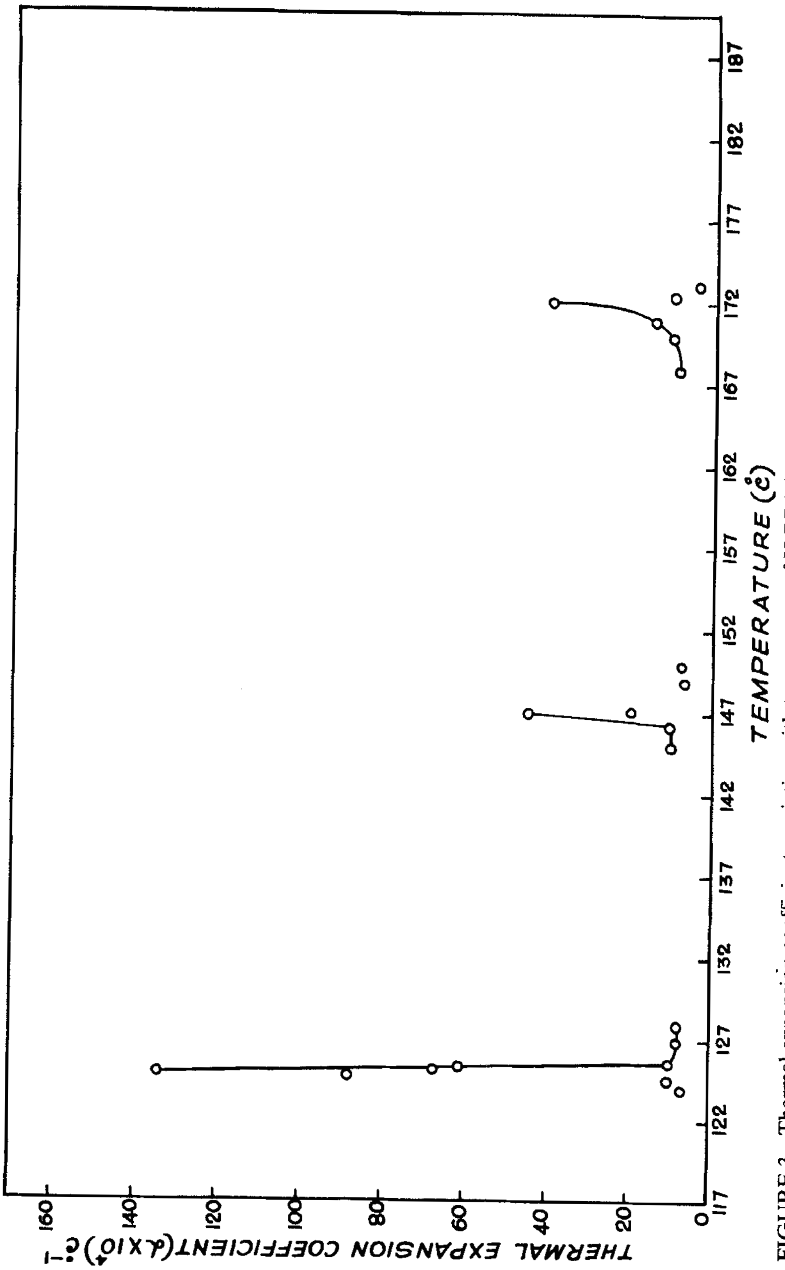


FIGURE 3 Thermal expansion coefficients variation with temperature of H_xBPAA.

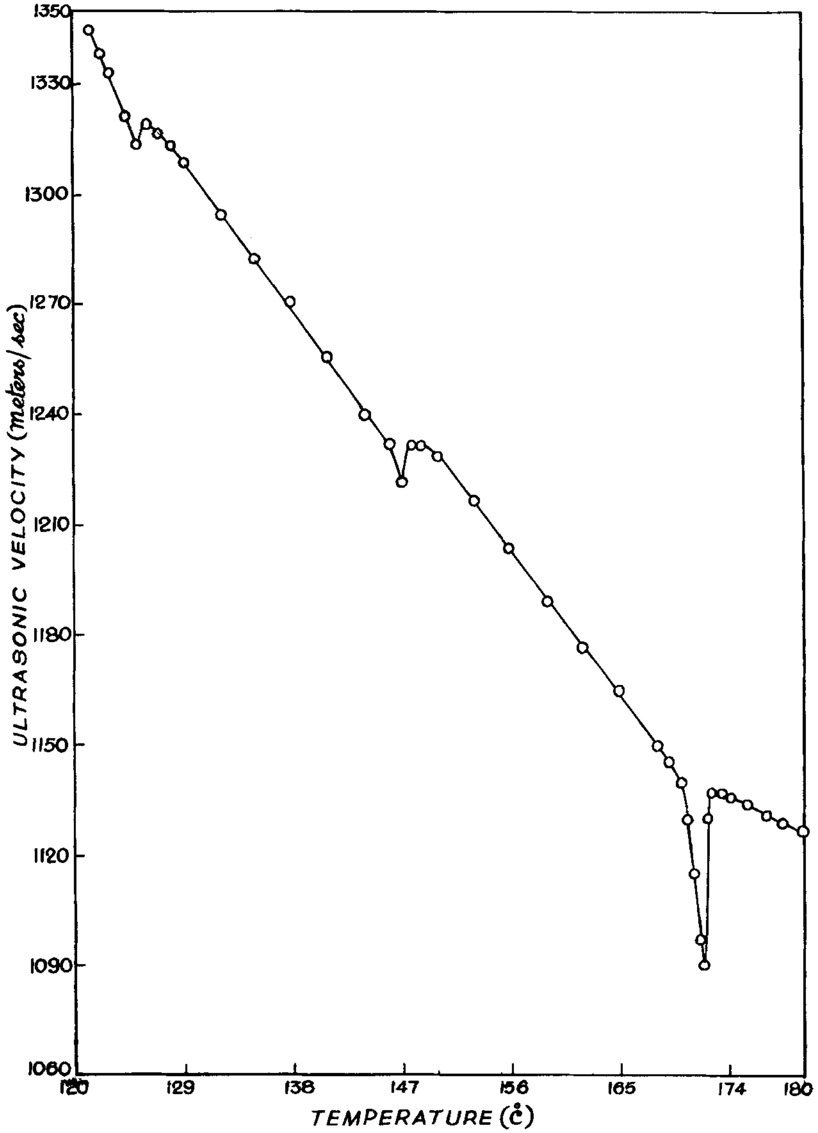


FIGURE 4 Ultrasonic velocity variation with temperature of H_xBPAA.

ficient at the isotropic liquid—nematic transition is 40.0 × 10^{-4}/°C. The jump in density and the high value of 'α' indicate that the isotropic liquid—nematic transition is probably of first order. The sudden jump in density at the transition is attributed to a sudden change in the molecular structure from the disordered isotropic liquid phase to the ordered nematic phase. The higher values of thermal expansion coefficients in the nematic phase than that of in the isotropic liquid phase indicate the tendency of increasing order with decrease of temperature is more in the nematic phase.[13,14,15] The breadth of the isotropic liquid—nematic transition is 1.6°C. Pretransitional effects at the isotropic liquid—nematic transition are found to occur markedly on the lower side of the transition[13,14] supporting the Maier-Saupe theory.[16]

After the isotropic liquid—nematic transition, density increases linearly with decrease of temperature in the nematic phase. At nematic—smectic A transition the density shows a sudden raise. The thermal expansion coefficient at nematic—smectic A transition is $45.4 \times 10^{-4}/°C$. The density jump and the thermal expansion coefficient indicate that the transition is probably of first order. Our measurements are in accordance with Torza and Cladis[17] on CBOOA. Some controversies are reported in literature whether the nematic—smectic A transition is of first order or second order. A good amount of theoretical work was also reported.[18,19] Cabane and Clark[20] showed that nematic—smectic A transition is of first order from DSC measurements. De Jeu[21] reported from studies of the heats of transition on di-*n*-hexyl, heptyl and octyl azoxybenzenes that the nematic—smectic A transition is of first order, weakly first order and second order, respectively.

Density increases linearly with decrease of temperature in the smectic A phase. Abrupt jump in density is observed at the smectic A—smectic B transition. The density jump across this transition is more predominant than the other transitions. The thermal expansion coefficient at this transition is $134.1 \times 10^{-4}/°C$. Hence the smectic A—smectic B transition can be of first order.

From the specific volume ($1/\rho$) jump at the isotropic liquid—nematic transition and from the tables of Maier—Saupe[22] which represent the variation of S_k and $A/KT_kv^2_{n,k}$ with $\Delta v/v_{n,k}$ we have calculated S_k, the degree of order and A the characteristic constant of the substance as 0.442 and 42.52×10^{-9}erg Cm^6 respectively.

The ultrasonic velocity increases with decrease of temperature in the isotropic liquid phase. With decrease of temperature the mean distance between the molecules decreases, which leads to an increase in the potential energy of interaction and to the observed increase in velocity. Just above the isotropic liquid—nematic transition temperature the ultrasonic velocity decreases and a minimum occurs at the isotropic liquid—nematic transition temperature. After the isotropic liquid—nematic transition a further decrease in temperature leads to an increase in ultrasonic velocity in the nematic region. The anomalous behaviour in velocity is observed for a temperature interval of ≈2.1°C. It is well established that the ultrasonic velocity is related to molecular structure and the nature of intermolecular interactions.[23] At the isotropic liquid—nematic transition the disordered isotropic liquid phase is converted to the ordered nematic phase and hence an anomalous behaviour is observed at the isotropic liquid—nematic transition. The ultrasonic velocity increases with decrease of temperature in the nematic phase because of the increase of molecular order among the molecules in the nematic phase.

Adiabatic compressibility decreases with decrease of temperature in the isotropic liquid phase, but a sudden jump is noticed in the adiabatic compressibility at the isotropic liquid—nematic transition. Figures 5 and 6 reveal that the Rao number and molar compressibility

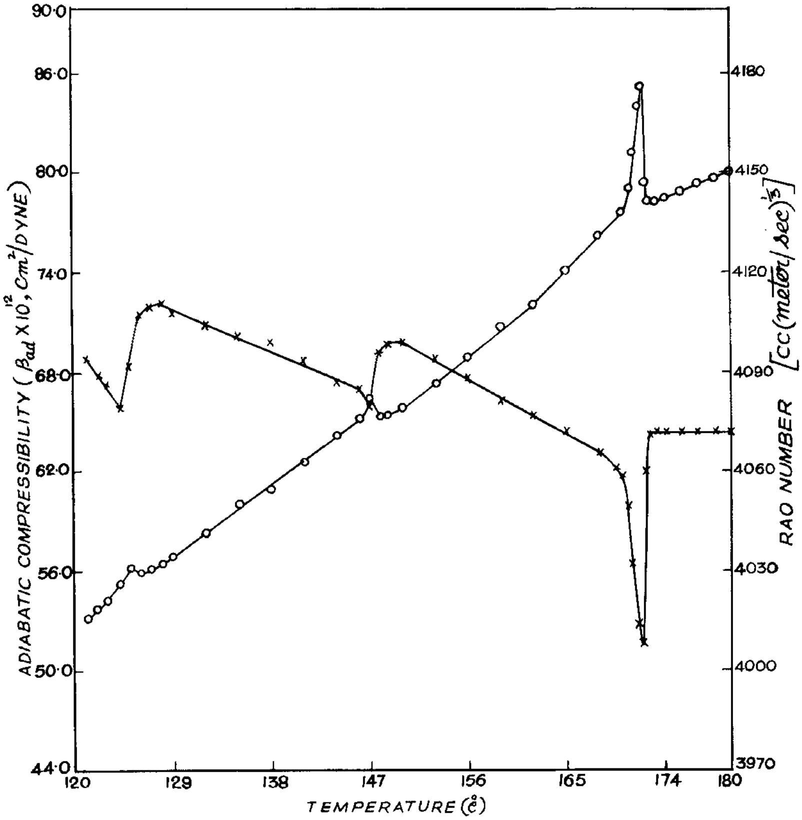


FIGURE 5 Adiabatic compressibility (0 – 0) and Rao number (× – ×) variation with temperature of H_xBPAA.

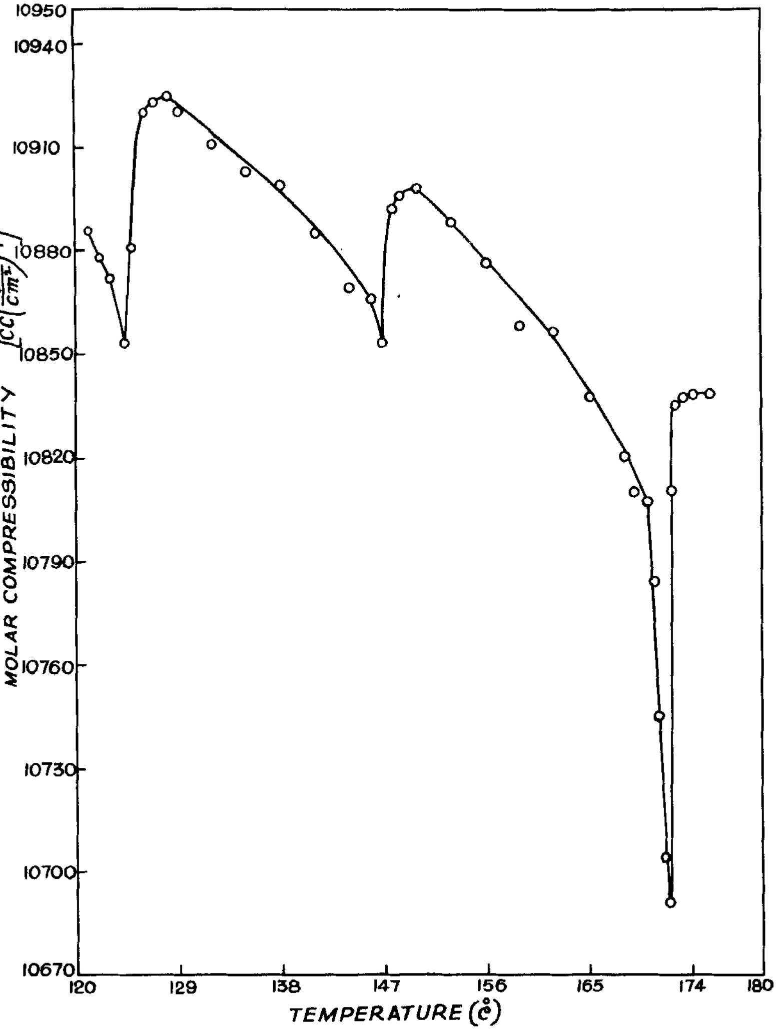


FIGURE 6 Molar compressibility variation with temperature of H_xBPAA.

are constant with decrease of temperature in the isotropic liquid phase, but a minima in Rao number (Molar sound velocity) and molar compressibility are observed at the isotropic liquid—nematic transition. The variation of β_{ad}, R_n and B reflect the pretransitional effects in ultrasonic velocity on both sides of the transition which can be explained on the basis of Frenkel's heterophase fluctuation theory.[24]

Small dips in ultrasonic velocity are observed at the nematic—smectic A and smectic A—smectic B transitions. At nematic—smectic A and smectic—smectic transitions the order changes very little and the temperature has less effect on the degree of order. So the velocity changes are small at the nematic—smectic A and smectic A—smectic B transitions.

Jumps in adiabatic compressibility and dips in Rao number and molar compressibility are observed at nematic—smectic A and smectic A—smectic B transitions.

Acknowledgments

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